*Aceh Int. J. Sci. Technol., 9(2) 90-101*
*August 2020*
*doi: 10.13170/aijst.9.2.17565*

**Aceh International Journal of Science and Technology**
**ISSN: p-2088-9860; e-2503-2398**
**Journal homepage: http://jurnal.unsyiah.ac.id/aijst**

# Charge Characteristics and Cation Exchanges Properties of Hilly Dryland Soils Aceh Besar, Indonesia

**Sufardi Sufardi[1*], Teti Arabia[1], Khairullah Khairullah[1], Zainabun Zainabun[1], Karnilawati Karnilawati[2], Sahbudin Sahbudin[1]**

[1]Department of Soil Science, Faculty of Agriculture, Universitas Syiah Kuala, Darussalam, Banda Aceh, Indonesia.
[2]Department of Agrotechnology, Faculty of Agriculture, Universitas Djabal Ghafur, Sigli, Indonesia
[*] Corresponding author email: sufardi_usk@unsyiah.ac.id

Received: July 28, 2020
Accepted: August 23, 2020
Online : August 31, 2020

**Abstract -** Soil surface charge and cation exchange are important parameters of soil fertility in tropical soils. This study was conducted to investigate characteristics of surface charges and cation exchanges on four soil orders of the dryland in Aceh Besar district. The soil order includes Entisols Jantho (05°16'58.41" N; 95°37'51.82" E), Andisols Saree (05°27'15.6" N; 95°44'09,1" E), Inceptisols Cucum (05°18'18,37" N; 95°32'48,04" E), dan Oxisols Lembah Seulawah (05°27'19,4" N; 95°46'19,2" E). The charge characteristics of surface charge are evaluated from the parameter of ΔpH ($pH_{H2O}$-$pH_{KCl}$), variable charge (Vc), permanent charge (Pc), and point of zero charges (PZC). In contrast, cation exchange properties are evaluated from several soil chemical properties, such as soil organic matter (SOM), base saturation (BS), cation exchange capacity (CEC), and effective CEC ($E_{CEC}$). The results show that the four pedons of soil in the hilly dryland of Aceh Besar include a variable charge because it has a PZC, which is characterized by a negative surface charge with a PZC of < $pH_{H2O}$ and has CEC dependent soil pH. PZC value varies from 3.21 – 5.26 and sequentially PZC Andisols > Oxisols > Entisols > Inceptisols. The total CEC value differs considerably from ECEC and the sum of cations. CEC total of the soils varies from 12.8 – 34.4 cmol $kg^{-1}$, whereas the ECEC values vary from 2.72 – 8.66 cmol $kg^{-1}$. The highest variable charge percentage is found in Andisols Saree. In contrast, the highest permanent charge is found in Inceptisols Cucum and is positively correlated with $pH_{H20}$, PZC, CEC, and sums of cations or ECEC. Improving soil quality in hilly dryland soils in Aceh Besar District can be done by decreasing the PZC status of soils with organic amendments and fertilizers or increasing the pH by using liming.

**Keywords**: Point of zero charges, cation exchange, dryland, soil order

## Introduction

Indonesia is a developing country that still relies on agriculture as a driver of the community's economy, especially residents in rural areas. However, with the increased conversion of rice fields to residential or urban land, the agricultural sector will face a challenge, especially in maintaining national food security. To anticipate the reduction in agricultural land, one of the great opportunities could be expanding the agriculture land by optimizing the acid dry and marginal land with an area of more than 140 million ha (Mulyani et al., 2010). Furthermore, of the total dryland area, 102 8 million hectares (69%) are acid soils (Hidayat and Mulyani, 2005). Oxisols, Aridisols, Alfisols, Ultisols, Inceptisols, and Entisols are predominant soils in the tropics, but the distribution of these soils are relatively varied among ecologies (Lal, 2019).

Many soils in the humid tropical climate are dominated by Inceptisols, Ultisols, Alfisols, and Oxisols (Uehara and Gillman, 1985). In Indonesia, these soils are mostly found in Sumatera, Kalimantan, and Papua, which predominantly dominate hilly and mountainous areas (Murtilaksono and Anwar, 2014). The drylands are generally less potential for crop farming due to low fertility rates, steep slopes, and shallow solum and low content and distribution of organic C (Fajrina et al., 2018, Sufardi et al., 2018). Despite low soil fertility rates, currently dryland has been used for agriculture for food, horticulture, plantations, and grazing land, as found in the hills of Aceh Besar District, Indonesia (Sufardi et al., 2019a). The research conducted by Martunis et al. (2016) shows that soil quality in Aceh Besar drylands varies from low to moderate, with low-quality soil is more dominant, especially in hilly areas. Similar results have also been reported by Helmi et al. (2017), which shows that parts of Aceh Besar dryland turned out to have generally low quality. Some soils in the tropical dryland have a low pH (<6.5), low base saturation (<50%), low organic matter content, high Al saturation, high P nutrient fixation (Mahesh et al., 2018, Sanchez, 2019, Whitley et al., 2019). Naturally, the decrease rate of soil organic matter in the tropics can reach 30-60% for ten years (Abdurrahman, 2008). The drop in soil organic matter content is not only due to the mineralization process that accelerates the degradation of soil carbon but also due to sloping land conditions so that erosion and nutrient loss are inevitable (Mani et al., 2018, Robertson et al., 2018).

Soil quality is not only specified by the physical and chemical properties of the soil but also is heavily influenced by the composition of clay minerals and organic matter content. Soils in tropical regions having strongly weathered, their mineral clay is generally dominated by mineral type 1:1 such as kaolinite and halloysite. At the same time, some fractions are occupied by oxide-hydroxide Al, Fe, and Si (Sanchez (2019. The content of kaolinite and gibbsite tends to increase as soil develops (Pincus et al., 2017). The study by Sufardi et al. (2019b) also reported that the Fe-oxide fraction is prevalent in developed soils such as Oxisol and Ultisols. The higher the $Fe_2O_3$ content, the higher the positive charge in tropical soils (Jiang et al., 2011). Therefore, it will increase the point of zero charge (PZC) due to the reduction of negative soil charge on the colloid surface (Huang et al., 2016, Kautsar et al., 2018, Moghimi et al., 2013).

Surface charges of soil colloid are closely related to the properties of cation exchange (Uehara and Gillman, 1985). For soils with high PZC, several problems will emerge from the physicochemical aspects of the soil, such as P fixation and low soil CEC due to low clay activity. The other issue also includes the easily leached nutrient cations such as Ca, Mg, K, and $NH_4$, so that nutrient availability is limited (Sanchez, 2019). For that reason, the study of the properties of charge and ion exchange of soil is pivotal in determining the strategy of soil management in tropical dryland farming, particularly in variable charge soils (Sandrawati et al., 2018). Soil surface charges affect the chemical properties of soil by varying the quantity of electric and surface charge density. Moreover, surface charge properties have a vital role in the migration of ions in the soil, the formation of organo-mineral complexes, soil structure, plant nutrition, and the dispersion, flocculation, swelling, and shrinkage of the soil fractions (Uehara and Gillman, 1985). Based on differences in the surface charge properties, soils can be classified into two basic categories: permanent-charge soils and variable-charge soils (Wen et al., 2020).

Most studies on soil surface charge properties were conducted in tropical and subtropical regions where the soils are poor and low in the negative charge. The electrochemical properties of soils are valuable fundamental knowledge in solving the fertility problems of soils of the tropical regions. The objectives of this study were to determine the characteristics of the charge and cation exchange in hilly soils of Aceh Besar, Indonesia.

## Materials and Methods

### Description of the study area

The study area is located in Aceh Besar District, Aceh Province, Indonesia, and geographically situated between 5° 2' – 5°, 8' N latitude and 95° 80' – 95°,88' E longitude. The climate is tropics with an average annual precipitation of about 1,251-1,426 mm/year and an average air temperature of 23-27$^{0}$C, which is classified as a dry climate because the dry season lasts 3-4 months in a year (BPS Aceh Besar, 2019). Based on the climate classification, according to Schmidt-Ferguson, most of this region in Aceh Besar District is included in type C, which is slightly wet. While based on Oldeman's study, this region is included in type E, with the characteristics of this area is generally too dry (BMKG, 2019). The temperature regime is hyperthermic with udic and ustic moisture regimes (Sufardi *et al*., 2018).

This study is focused on dryland areas in Aceh Besar District (Indonesia), which represent several soil orders, including Entisols, Andisols, Inceptisols, and Oxisols (Figure 1). The district also represents four types of parent material, which are weathered bedrocks, volcanic ash, sandy sedimentary rock, and andesitic-basaltic tuff (Sufardi *et al*., 2018). The current land use of the dryland area encompasses scrub forest, horticultural garden, mixed plants, moor, grazing land, and land where currently cultivates maize, soybean, peanut, long bean, watermelon, cassava, fruits, and vegetables as essential crops (McLeod *et al.*, 2019). Four pedons were selected among the dug profiles representing parent materials and soil orders by the geopedology approach. Then, these different soil horizons were sampled for laboratory analysis. The morphological properties of the soils were described in the field (Bogor Soil Research Centre, 2014) and were classified according to the USDA Soil Taxonomy (Soil Survey Staff, 2014).

**Soil chemical analysis**

Field study and sample collection were carried out from May to July 2018. The soil samples were air-dried and sieved with a 2-mm sieve for texture analysis and 0.5-mm for soil chemical analysis. Before the analysis, the soil samples were kept in plastic bags. Soil organic matter (SOM) content was determined by the wet combustion procedure of Walkley and Black (Buurman 1996). The pH was measured in the supernatant suspension of 1 : 2.5 soil : water suspension ($pH_{H2O}$), and 1 : 2.5 soil : 1 M KCl solution ($pH_{KCl}$) (Soil Research Centre 2005). Electrical conductivity (EC) was measured by electrical conductivity-meter in the water suspension of 1:5 soil: water. Exchangeable cations and cation exchange capacity (CEC) of the soils were determined by the 1 M ammonium acetate (pH 7) method. The exchangeable cations ($Ca^{2+}$, $Mg^{2+}$, $K^{+}$, and $Na^{+}$) in the leachate were determined by the atomic absorption spectrophotometer (AAS, Shimadzu 7000). Exchangeable acidity ($Al^{3+}$ + $H^{+}$) of soils were extracted by 1M KCl in the ratio soil: extractant of 1:10 and measured with the titration method (McLean 1965). Effective CEC or ECEC was calculated from the sum of base cations ($Ca^{2+}$ , $Mg^{2+}$, $K^{+}$ and $Na^{+}$) with acid cations ($Al^{3+}$ + $H^{+}$), whereas base saturation (BS) was calculated by formula: BS = (ΣCa+Mg+K+Na/CEC x 100%) (van Reeuwijk, 2006) and Al saturation was calculated by formula: Al saturation ($Al_{sat.}$) = exch. Al/ECEC x 100% (Fageria *et al.* 2016).

**Determination of point of zero charge**

The point of zero charges (PZC), denoted as $pH_{0,}$ was determined by the method of Gillman and Sumner (1987). Six portions of 2 g of 2 mm air-dried samples were weighed into 50 mL plastic centrifuge tubes and shaken with 20 mL of 0.1 M $CaCl_2$ for 2 hours to saturate the soil with Ca. The suspension was centrifuged (3000 rpm, 10 min), and the supernatant was discarded. The Ca saturated soil was washed twice with 20 mL of 0.002 M $CaCl_{2,}$ and after the third adding of 20 mL of 0.002 $CaCl_2$, the pH was adjusted to six values of 0.1 M HCl in the range of 3.5 to 6 mL by dropwise addition. Equilibration of the pH took several days. When equilibrium occurred for 0.002 M $CaCl_2$, the pH was recorded as $pH_{0.002}$. Then, 0.5 mL of 2 M $CaCl_2$ was added to each sample and shaken for 3 hours. Later, the pH was recorded and designated as $pH_{0.05}$. For each tube, pH was calculated as ($pH_{0.05}$ - $pH_{0,02}$). The $pH_0$ was obtained from the plot of pH against $pH_{0.002}$. The $pH_0$ was identified as the point where pH was zero.

**Charge characteristics**

Characteristics of soil colloids are evaluated from the ΔpH value, which is the difference between $pH_{KCl}$-$pH_{H2O}$ and the difference from the value of $pH_0$-$pH_{H2O}$ (Uehara and Gillman 1985). In contrast, the variable charge (Vc) is calculated from the CEC potential (1N ammonium acetate pH7 method) minus the effective CEC (Gillman, 2007). The percentage of permanent charge (Ppc) is calculated from the formula: [ECEC/CEC] x 100%, while the percentage of variable charge (PVc) = (Vc)/CEC x 100% (Uehara and Gillman, 1985). Finally, the assessment of chemical properties is using criteria from the Soil Research Center (2005).

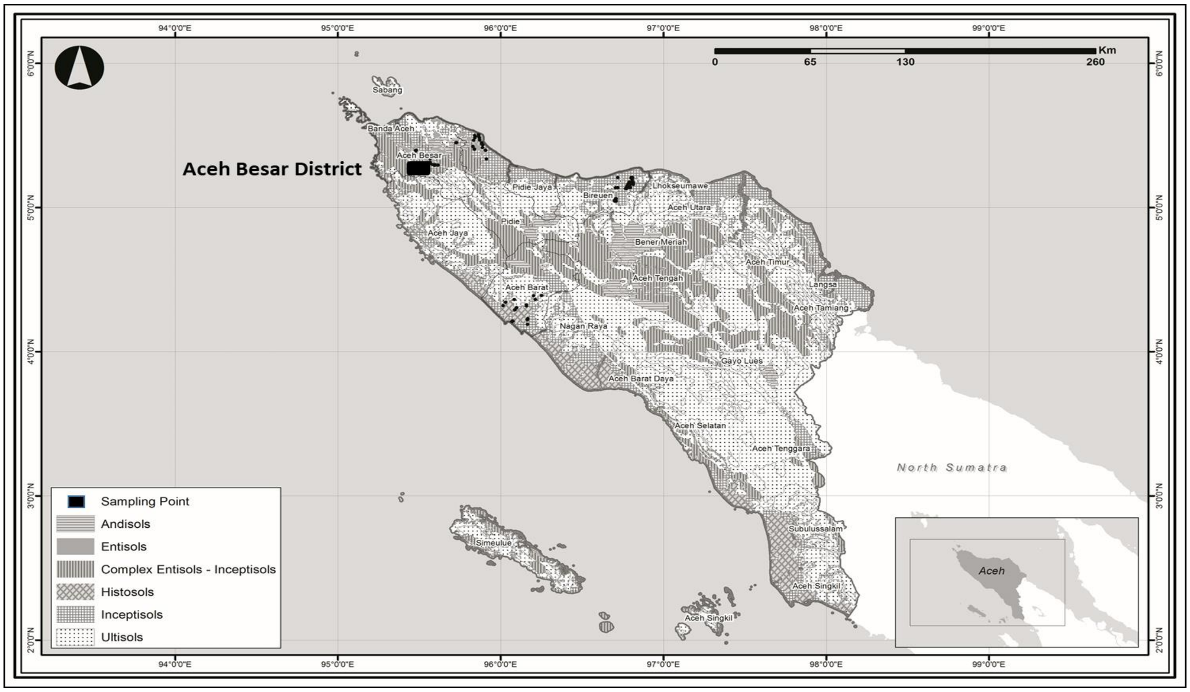


Figure 1. Soil order map of Aceh (BPN Aceh 2017, unpublished)

## Results

### Soil description

Based on the soil profile observations, soil analysis, and clay mineral analysis, the classification of soil subgroups from four soil profiles from the hilly dryland of Aceh Besar District is presented in Table 1.

Table 1. Classification of soil subgroup according to Soil Survey Staff (2014) of four soil pedons in hilly dryland of Aceh Besar District

| Pedon | Site/Location | Soil classification (USDA, 2014) | Relief | Parent materials | Land use |
|---|---|---|---|---|---|
| P1 | Jantho | Coarse loamy, mixed, udic, isohyperthermic, Typic Udorthents | Hilly | Weathered rocks | Shrubs |
| P2 | Saree | Fine loamy, allophanic, udic, isohyperthermic, Eutric Hydrudands | flat | Volcanic ash | Horticulture land |
| P3 | Cucum | Fine silty, mixed, udic, isohyperthermic, Oxic Dystrudepts | Sloping | Sedimentary rocks | Grazing land |
| P4 | Lembah Seulawah | Fine (clay), ferritic, udic, isohyperthermic, Plintic Kandiudox. | Hilly | Andesitic-basaltic | Mixed farming |

Source: Field identification (adapted from Sufardi *et al*. 2018)

There are four pedons (P1, P2, P3, and P4) and soil subgroups developed in the dryland of Aceh Besar, namely: Typic Udorthents (Entisols), Eutric Hydrudands (Andisols), Oxic Dystrudepts (Inceptisols), and Plinthic Kandiudox (Oxisols). These soils are mostly found in the humid climate (udic) regime with the isohyperthermic temperature regime. The mineral composition in the soil is varied between soil orders and generally consists of mixed minerals, which are a mixture of primary and secondary minerals (Apriani *et al*., 2019). From Table 1, it can be seen that the texture of the topsoil of Aceh Besar drylands varies from fine to medium, while the arrangement of the horizon also varies. Based on the composition of the horizon, the undeveloped soil is Entisols because it is composed of horizon A, AC, and C with the thickness of the solum <50 cm, while the others relatively have developed because it horizonization process has occurred to generates more horizons.

*doi: 10.13170/aijst.9.2.17565*

The undeveloped soils are Entisols Jantho, whereas newly developing soil groups are Inceptisols Cucum and Andisols Saree, and, while the group that has developed further is Oxisols Lembah Seulawah.

**Soil pH, SOM, BS, and exchange acidity**

Table 2 shows that the soil pH $H_2O$ of four soil orders at all horizon layers is between 5.25-6.72, while pHKCl ranges from 4.01-5.64. The table also shows that in the four soil pedons studied, it has an average low SOM content (<20 g $kg^{-1}$) or less than 2%, except in the P2 soil pedon or Eutric Hydrudands (Andisols) Saree. In this Andisols Saree, organic C content ranges from 9.40-39.5 g $kg^{-1}$ or 0.94 to 3.95%. This organic C content varies from very low to moderate. In other soils (pedon P1, P3, and P4), they have very low organic C content of 2.3-6.4 g $kg^{-1}$ or 0.23-0.64%. The value of soil EC in all horizon layers of the four soil orders are classified as very low (0.01 - 0.05 dS $m^{-1}$), while base saturation varies from very low to low (6.80-29.5%). Furthermore, soil exchange acidity ($Al^{3+}$ and $H^+$) of the soils is included in the low criteria except at the Ap horizon of Inceptisols (Oxic Dystrudepts), which is 2.40 cmol $kg^{-1}$ of $Al^{3+}$ and 1.20 cmol $kg^{-1}$ of $H^+$.

Table 2. Soil chemical properties at horizon layers of the soils studied in Aceh Besar district

| Pedon /Subgroup | Horizon/ Depth (cm) | $pH_{H2O}$ | $pH_{KCl}$ | SOM (g $kg^{-1}$) | EC (dS $m^{-1}$) | BS (%) | EA (cmol $kg^{-1}$) | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | $Al^{3+}$ | $H^+$ |
| P1 | Ap/0 – 20 | 6.41 | 4.41 | 5.10 | 0.02 | 19.3 | 0.00 | 0.24 |
| Lithic Udorthents. | AB/20–38 | 6.72 | 4.82 | 3.04 | 0.01 | 19.3 | 0.00 | 0.24 |
| Jantho | Bw/38–60 | 5.30 | 4.75 | 4.40 | 0.02 | 12.2 | 0.80 | 1.00 |
| P2 | Ap/0 – 20 | 5.56 | 5.05 | 39.5 | 0.05 | 10.6 | 0.48 | 0.72 |
| Eutric Hydrudands. | AB/20–38 | 5.87 | 5.39 | 14.2 | 0.02 | 16.6 | 0.00 | 0.32 |
| Saree | Bw/38–60 | 6.06 | 5.64 | 9.80 | 0.02 | 18.6 | 0.00 | 0.24 |
| | BC/60–130 | 5.25 | 4.79 | 9.40 | 0.03 | 16.3 | 0.24 | 0.60 |
| P3 | Ap/0 - 19 | 5.45 | 3.95 | 6.40 | 0.03 | 18.8 | 2.40 | 1.20 |
| Oxic Dystrudepts. | AB/19–42 | 5.74 | 4.01 | 4.60 | 0.03 | 21.5 | 1.60 | 0.88 |
| Cucum | BA/42–70 | 6.10 | 4.36 | 4.50 | 0.04 | 29.5 | 0.00 | 0.32 |
| | Bw1/70-110 | 5.96 | 4.41 | 2.80 | 0.06 | 28.6 | 0.00 | 0.32 |
| | Bw2/110-130 | 6.96 | 5.33 | 2.30 | 0.06 | 17.2 | 0.00 | 0.24 |
| P4 | A/0 – 10 | 5.43 | 4.82 | 4.80 | 0.02 | 16.5 | 0.24 | 0.64 |
| Plintic Kandiudox. | AB/10 – 35 | 5.58 | 5.24 | 4.50 | 0.04 | 17.4 | 0.00 | 0.68 |
| Lembah Seulawah | BA/35 – 69 | 5.40 | 5.07 | 3.60 | 0.04 | 6.80 | 0.24 | 0.68 |
| | Bo1/69–104 | 5.36 | 5.00 | 3.40 | 0.02 | 15.2 | 0.48 | 0.60 |
| | Bo2/104-150 | 5.44 | 4.81 | 9.90 | 0.02 | 7.07 | 0.00 | 0.40 |

SOM=soil organic matter, EC=electrical conductivity, BS=base saturation, EA=exchangeable acidity

**Charge characteristics**

The results of the analysis of several parameters related to the colloid charge characteristics of the four soil pedons in the Aceh Besar hilly drylands showed that all the soils included variable charge soils because all soils had points of zero charge (PZC). Table 3 reveals that PZC values vary from 3.21 - 5.26. Generally, the highest values are found in pedons P2 (Eutric Hydrudands, Saree) and P4 (Plintic Kandiudox, Seulawah Valley). In pedon P1 (Lithic Udorthents, Jantho) and P3 (Oxic Dystrudepts, Cucum), the value of PZC is comparatively lower because the soils are consisting of mixed mineral compositions. The value of ΔpH of four soil pedons, ranges from -0.33 to -2.00 and the value of PZC-pH ranges from -0.10 to – 3.26 and all they have values negative. From Table 3 also shows that on the four orders of soil in the dryland of Aceh, Besar has a variable charge greater than the permanent charge. Variable charges (Vc) on all of the soil profile studied range from 11.1 – 31.9 cmol $kg^{-1}$, while permanent charge (pc) ranges from 2.72 – 8.66 cmol $kg^{-1}$). Variable charge percentages range from 63.8 – 86.6% while permanent charge range from 9.40 – 36.9%. Based on the data, the four orders of soil on the hilly dryland of Aceh Besar is categorized as variable charge soils.

Table 3. Charge characteristics at horizon layers of the soils studied in Aceh Besar district

*doi: 10.13170/aijst.9.2.17565*

| Pedon /Subgroup | Horizon/ Depth (cm) | PZC | ΔpH | PZC-pH | Vc | pc | PVc | Ppc |
|---|---|---|---|---|---|---|---|---|
| | | | | | ---(cmol kg$^{-1}$)--- | | ------ (%) ------ | |
| P1 | Ap/0 – 20 | 3.21 | -2.00 | -3.20 | 27.5 | 6.89 | 86.6 | 13.4 |
| Lithic Udorthents, | AB/20–38 | 3.46 | -1.90 | -3.26 | 26.2 | 6.58 | 80.0 | 20.0 |
| Jantho | Bw/38–60 | 3.63 | -0.55 | -1.67 | 26.0 | 5.64 | 79.9 | 20.1 |
| P2 | Ap/0 – 20 | 3.91 | -0.51 | -1.65 | 24.9 | 4.30 | 82.2 | 17.8 |
| Eutric Hydrudands, | AB/20–38 | 5.01 | -0.48 | -0.86 | 20.7 | 4.50 | 85.3 | 14.7 |
| Saree | Bw/38–60 | 5.14 | -0.42 | -0.92 | 21.3 | 5.15 | 82.1 | 17.9 |
| | BC/60–130 | 4.12 | -0.46 | -1.13 | 13.6 | 3.64 | 80.5 | 19.5 |
| P3 | Ap/0 - 19 | 3.47 | -1.50 | -1.98 | 13.3 | 7.52 | 70.1 | 29.9 |
| Oxic Dystrudepts, | AB/19–42 | 3.83 | -1.73 | -1.91 | 16.1 | 7.55 | 63.8 | 36.2 |
| Cucum | BA/42–70 | 4.21 | -1.74 | -2.89 | 16.9 | 7.52 | 68.0 | 32.0 |
| | Bw1/70-110 | 3.86 | -1.55 | -2.10 | 20.5 | 8.66 | 69.2 | 30.8 |
| | Bw2/110-130 | 4.21 | -1.63 | -2.75 | 23.0 | 5.05 | 70.3 | 29.7 |
| P4 | A/0 – 10 | 3.94 | -0.61 | -1.49 | 10.8 | 3.19 | 78.8 | 21.2 |
| Plintic Kandiudox, | AB/10 – 35 | 4.48 | -0.34 | -1.10 | 11.2 | 3.19 | 77.2 | 22.8 |
| Lembah Seulawah | BA/35 – 69 | 4.45 | -0.33 | -0.95 | 31.9 | 3.31 | 77.8 | 22.2 |
| | Bo1/69–104 | 5.26 | -0.36 | -0.10 | 11.1 | 3.27 | 90.6 | 9.40 |
| | Bo2/104-150 | 4.24 | -0.63 | -1.20 | 30.1 | 2.72 | 77.3 | 22.7 |

Vc = variable charge, pc = permanent charge, PVc = variable charge percentage,
Ppc = permanent charge percentage

**Cation exchange properties**

In Table 4, it can be observed, in general, the sum of $Ca^{2+}$, $Mg^{2+}$, $K^{+}$, and $Na^{+}$ cations (1N $NH_4OAc$ pH7 extract) on each horizon layer of the four soil pedons of Aceh Besar at the hilly drylands is different between pedons or soil subgroups. The values vary from 2.19 - 8.34 cmol kg$^{-1}$ (very low to moderate). Based on the Bogor Soil Research Center (2005) criteria, the exch content. Ca of all horizon layers analyzed vary from very low to moderate (1.56 - 7.52 cmol kg$^{-1}$), whereas exch. Mg is very low. The content of exch. K ranges from very low to low (0.03-0.38 cmol kg$^{-1}$) and exch. Na is classified as low (0.18-0.35 cmol kg$^{-1}$). The data in the table shows that most of the soils in hilly drylands of Aceh Besar (for all pedons) are classified as low, especially for Mg, K, and Na, and Ca content in P4 (Plintic Kandiudox) Lembah Seulawah. When viewed on each pedon, P3 pedons (Oxic Dystrudepts, Cucum) and P1 pedons (Lithic Udorthents, Jantho) have a relatively higher number of base cations (Ca, Mg, K, and Na) than those in P2 pedons (Eutric Hydrudands, Saree) and P3 (Plintic Kandiudox, Lembah Seulawah). This result is due to the soil order in pedon P1, and P3 belongs to the undeveloped soil when compared to the soil in pedon P2 and P4. Table 4 also demonstrates that the cation exchange capacity (potential CEC and effective CEC) varies between the soil pedons studied. Potential CEC values vary from low to high (12.8 - 34.4 cmol kg$^{-1}$) while ECEC varies from very low to moderate (2.72 - 8.66 cmol kg$^{-1}$).

**Correlation between soil chemical parameters**

Pearson correlation matrix analisis between the characteristics of the charge with some soil chemical properties show very significant correlation between the soil colloids charge with some soil chemical properties, e. g the number of base cations (SC), CEC, ECEC, base saturation, and pH $H_2O$. Ssoil with characteristics such as charge values of ΔpH, PZC-pH, and permanent charge (pc) show no correlation with PZC, variable charge (Vc), pH KCl, and soil organic matter (Table 5). Thii result also indicates that the number of cations bound to colloids, cation exchange capacity, and base saturation of soils in the hilly dryland of Aceh Besar depends on the amount of charge on the surface soil colloid, especially the amount of negative charge. However, these numbers are not influenced by a large number of variable charges. The difference between PZC-pH and ΔpH (pH KCl– pH $H_2O$) is negatively correlated with soil CEC value, whereas the permanent charge (pc) and pH$H_2O$ are positively correlated.

Table 4. Exchangeable cations, and cation exchange capacity at horizon layers of the soils studied in Aceh Besar district

| Pedon /Subgroup | Horizon/ Depth (cm) | Exchangeable Cation | | | | Sum of cations | $CEC_p$ | $E_{CEC}$ |
|---|---|---|---|---|---|---|---|---|
| | | Ca | Mg | K | Na | | | |
| | | ---------- | ---------- | ---------- | (cmol kg$^{-1}$) | ---------- | ---------- | ---------- |
| P1 | Ap/0 – 20 | 6.10 | 0.31 | 0.03 | 0.21 | 6.65 | 34.4 | 6.89 |
| Lithic Udorthents, | AB/20–38 | 5.78 | 0.31 | 0.03 | 0.22 | 6.34 | 32.8 | 6.58 |
| Jantho | Bw/38–60 | 3.08 | 0.34 | 0.24 | 0.18 | 3.84 | 31.6 | 5.64 |
| P2 | Ap/0 – 20 | 2.42 | 0.35 | 0.14 | 0.19 | 3.10 | 29.2 | 4.30 |
| Eutric Hydrudands, | AB/20–38 | 3.23 | 0.36 | 0.38 | 0.21 | 4.18 | 25.2 | 4.50 |
| Saree | Bw/38–60 | 4.14 | 0.36 | 0.19 | 0.22 | 4.91 | 26.4 | 5.15 |
| | BC/60–130 | 2.05 | 0.36 | 0.19 | 0.20 | 2.80 | 17.2 | 3.64 |
| P3 | Ap/0 - 19 | 3.09 | 0.39 | 0.09 | 0.35 | 3.92 | 20.8 | 7.52 |
| Oxic Dystrudepts, | AB/19–42 | 4.28 | 0.39 | 0.07 | 0.33 | 5.07 | 23.6 | 7.55 |
| Cucum | BA/42–70 | 6.40 | 0.38 | 0.09 | 0.33 | 7.20 | 24.4 | 7.52 |
| | Bw1/70-110 | 7.52 | 0.38 | 0.12 | 0.32 | 8.34 | 29.2 | 8.66 |
| | Bw2/110-130 | 4.19 | 0.31 | 0.09 | 0.22 | 4.81 | 28.0 | 5.05 |
| P4 | A/0 – 10 | 1.74 | 0.35 | 0.03 | 0.19 | 2.31 | 14.0 | 3.19 |
| Plintic Kandiudox, | AB/10 – 35 | 1.89 | 0.36 | 0.05 | 0.21 | 2.51 | 14.4 | 3.19 |
| Lembah Seulawah | BA/35 – 69 | 1.77 | 0.36 | 0.03 | 0.23 | 2.39 | 15.2 | 3.31 |
| | Bo1/69–104 | 1.56 | 0.36 | 0.03 | 0.24 | 2.19 | 14.4 | 3.27 |
| | Bo2/104-150 | 1.61 | 0.36 | 0.12 | 0.23 | 2.32 | 12.8 | 2.72 |

CECp = potential CEC, ECEC = effective CEC

Tabel 5. Pearson correlation coefficients between soil charge and cation exchange of soils from hilly dryland of Aceh Besar

| Soil chemical properties | SC | CEC | ECEC | PZC | ΔpH | PZC-pH | $p_c$ |
|---|---|---|---|---|---|---|---|
| SC | 1 | | | | | | |
| CEC | 0.738** | 1 | | | | | |
| ECEC | 0.883** | 0.674** | 1 | | | | |
| PZC | -0.374 | -0.463 | -0.529 | 1 | | | |
| ΔpH | -0.796** | -0.580 | -0.822** | 0.645** | 1 | | |
| PZC-pH | -0.733** | -0.679** | -0.682** | 0.754** | 0.898** | 1 | |
| Vc | 0.171 | 0.417 | 0.019 | -0.219 | -0.104 | -0.272 | |
| pc | 0.883** | 0.674** | 0.929** | -0.529 | -0.822** | -0.682** | 1 |
| $pH_{H2O}$ | 0.673** | 0.641** | 0.442 | -0.186 | -0.695** | -0.731** | 0.442 |
| $pH_{KCl}$ | -0.370 | -0.106 | -0.656** | 0.688** | 0.628** | 0.449 | -0.656** |
| SOM | 0.235 | 0.144 | -0.219 | 0.044 | 0.324 | 0.169 | -0.219 |
| Base saturation | 0.806** | 0.368 | 0.767** | -0.164 | -0.643** | -0.495 | 0.767** |

SC = sum of cations, CEC = cation exchange capacity, ECEC = effective CEC, Vc = variable charge, pc = permanent charge, PZC = point of zero charge, N = 17 (critical value: $\alpha_{0.01}$ = 0.615)

## Discussion

### Charge characteristics and its effect on soil fertility

Characteristics of charge on the surface of soil colloids are influenced by soil pH, clay mineral composition, soil texture, and soil organic matter content (Sposito, 2010). Therefore, the characteristics of soil colloid charge can also affect on soil fertility, especially the soils that develop in the tropics (Bohn et al., 2013). The results of the analysis of some soil chemical properties and charge characteristics showed that the quality of the soil in the hilly drylands of Aceh Besar is closely related to the characteristics of the soil charge.

Table 2 shows that some of the chemical properties analyzed, it can be seen that based on the pH$H_2O$ values of soil in the four pedons studied in the hilly dryland of Aceh Besar, they are generally classified as acidic soils because their pH is <6.50. Based on these pH values, the soils of the Aceh Besar hilly drylands need proper management and treatment as the pH value needs to be adjusted with the level of tolerance of the plant to be cultivated. Although these soils are classified as acidic, the highest Al-exchangeable (Al-exch.) levels are only found on the Ap horizon of the Oxic Dystrudepts (P3) Cucum, which is 2.40 cmol $kg^{-1}$. This result shows that the indication of Al toxicity only occurred in the soil of Inceptisols Cucum. For this soil, liming treatment is needed to decrease the exchangeable Al and raise the soil pH (Fageria 2016) or planting with tolerant crops (Sade et al. 2016, Kalkhoran et al. 2020). The need for the addition of lime or other amendment material to the four soils in the hilly dryland of Aceh Besar is justified because the analysis also shows that the base saturation (BS) of soils is in low criteria or less than 50 percent. At the same time, the EC value of the soil was also very low (<2.0 dS $m^{-1}$). Table 2 also shows that although there is a difference in the soil profile horizon, in general, the SOM content is low (<10 g $kg^{-1}$), and only in Andisols Saree that have moderate SOM content. A good soil ideally has soil organic matter content more of 30 g $kg^{-1}$ or 60 t $ha^{-1}$ (Mani et al., 2018). Hence, based on the data (Table 2), the four subgroups of soil found in hilly drylands of Aceh Besar District require amelioration with the addition of amendments in the form of organic matter or other soil amendments (Kalkhoran et al. 2020) and fertilization (Sufardi et al. 2018).

The point of zero charges (PZC), often denoted as $pH_0$, is one of the most crucial parameters used to describe variable-charge surfaces (Van Ranst et al., 2017). Uehara and Gillman [1985] indicated that $pH_0$ is the pH where the amounts of the negative and positive charge of variable charge components where these are equal. The previous study shows that the $pH_0$ values decrease with the increase of organic matter content and increase with the rise in sesquioxides (Pincus et al., 2017). This value is because the mineral composition of the two soils is dominated by Fe and Al oxide hydrate fractions, which have high PZC such as allophane, gibbsite, goethite (Oliver et al., 2019). Furthermore, if PZC values are observed at each horizon layer, it appears that the PZC in the upper soil layer is lower than the PZC in the lower soil layer. This result is because the upper layer has a higher organic matter content, which contributes to the low PZC of the soil (Khan and Kar, 2017).

Table 3 also shows that all the soils have a negative surface charge due to ΔpH and PZC-$pHH_2O$ values have a negative > 0.50. Uehara and Gillman (1985) mention that if the value of ΔpH calculated from the value difference of pHKCl and $pHH_2O$ has a negative difference more than 0.5, then the soil is negatively charged. Contrarily, if the difference is negative less than 0.5 or is positive, then the soil is positively charged (Tan, 2010). This negative difference is higher in soils than pedon P1 (Lithic Udorthents) and pedon P3 (Oxic Dystrudepts). The table also shows that the density of the variable charge is higher than the permanent charge so that the four soils can be included as soil with a variable charge system. The variable charge amount ranges from 11.1 - 30.9 cmol $kg^{-1}$ or 63.8 - 90.6%, while the permanent charge only ranges from 2.22 - 8.66 cmol $kg^{-1}$ or around 9.40-36.2%.

The permanent charge is the charge generated from the isomorphic substitution process on soil clay minerals, while the variable charge comes from the ion dissociation process on the colloid surface (Gillman, 2007; Tan, 2010). Sposito (2010) and Oliver et al. (2019) states that permanent charges are generally produced by 2: 1 clay minerals, while variable charges are formed by the ionization of functional groups of organic matter and Fe and Al oxide-hydroxide. Soil surface charges affect the chemical properties of soil by varying the quantity of electric and surface charge density (Uehara and Gillman, 1985). Surface charge properties have a significant bearing on the migration of ions in the soil, the formation of organomineral complexes, soil structure, plant nutrition, and the dispersion, flocculation, swelling, and shrinkage of the soil fractions (Sposito, 2010). Based on differences in the surface properties, soils can be classified into two basic categories: permanent-charge soils and variable-charge soils (Khan and Kar, 2017). The point of zero charges (PZC), often denoted as $pH_0$ is one of the most important parameters used to describe variable-charge surfaces (Uehara and Gillman, 1985).

From these two CEC values, it can be seen that the potential CEC is higher in value compared to the effective CEC. Also, there is a big difference between the potential CEC value and effective CEC. This difference is due to the four pedons of soils studied included in the soil with a variable charge. The charge on the variable colloidal surface of soils will always produce varying soil CEC values (Aprile and Lorandi, 2012; Gillman, 1987; Uehara and Gillman, 1985). The results of research on several soil orders in Aceh dryland also confirms that the potential CEC is higher than the effective CEC or real CEC (Kautsar et al., 2018, Sufardi et al., 2017, Sufardi et al., 2019). A high potential CEC value results from an increase in negative charge due to an increase in pH of the 1N $NH_4OAc$ extracting solution pH7 (Uehara and Gillman, 1985).

The CEC is defined as the ability of a particle to change positive bases with the environment in which the particle interacts. Cations can be exchanged for another positively charged ion from the surfaces of clay minerals and organic matter (Aprile and Lorandi, 2012). The CEC can directly influence the changes in soil pH because every time the clay particles capture cations, they release $H^+$ and $Al^{3+}$ ions, which acidifies soil when they are in high concentrations. Generally, tropical soils have low CEC, especially for high sandy and low pH soils. Minerals as oxides of aluminum, iron, and manganese that are very abundant in tropical soils also contribute to the low CEC. In these cases, more significant investment in fertilization, especially with humic compounds, becomes necessary.

This study shows that if the soil PZC value is lower than pH $H_2O$, then the soil tends to be negatively charged so that the soil CEC will increase. Likewise, if the value of ΔpH is getting negative, then the colloid surface of the soil is negatively charged (Tan, 2010), thus increasing CEC (Gillman, 1987). Soil CEC values also tend to increase with increasing pH $H_2O$ because between the two parameters, and there is a positive correlation. The results of the correlation analysis are by the concept or variable load theory proposed by Uehara and Gillman (1985), which states that the soils containing variable charge are strongly influenced by pH, electrolyte concentration, temperature, ion valence, and PZC-pH parameters. There is no significant correlation between soil CEC with the variable charge amount, PZC, and soil organic C content. This result is presumably because the variable charge generated in the soil fluctuates depending on the factors that affect surface charge density (Ueahara and Gillman, 1985). Organic matter is a contributor to variable charge so that the higher in the soil, the variable charge increases. This charge does not directly reflect the number of cations that are bound to the surface of the exchange complex (Aprile and Lorandi, 2012). This can be seen in Table 6, which shows that the value of potential CEC higher than ECEC.

**Implications for Soil Management**

The results of the study show that the four pedons of dry land in the hills of Aceh Besar are classified as variable soils, where the colloid charge was dominated by the variable charges with the amount more than 60% of the total charge of soil colloid (Uehara and Gillman 1985). This variable charge comes from two primary sources, namely Al and Fe oxide-hydroxide fractions and from organic material (Boh et al. 2013). This charge occurs because of the dissociation of ions ($H^+$ and $OH^-$) on the surface of clay minerals and on oxide-hydroxide of Al and Fe and ionization of functional groups of soil organic compounds (Khan and Kar, 2017) and this charge is influenced by pH (Bohn et al. 2013).

Furthermore, from the cation exchange properties shown by the low number of base cations, CEC, and effective CEC as well as relatively acidic soil pH, then the root cause of these problems is low clay soil activity. Th e lob number of CECE is because of soil composition is dominated by the oxide-hydroxide Al and Fe fractions and low content of organic matter (Apriani et al. 2019, Sufardi et al. 2019b). Thus, to improve soil quality, it is required to ameliorate or provide soil amendment. Based on the characteristics of the load and the problems above, one possible strategy is to provide organic amendments such as compost, manure, organic residues, biochar, green manure, and other materials. Several studies have shown that organic amendments generally have a high negative charge to increase cation exchange capacity (Cooper et al. 2020, Liu et al. 2020, Ramos et al. 2018) and are expected to reduce the soil PZC status (Uehara and Gillman 1985).

Organic matter has a very high CEC ranging from 250 to 400 meq/100 g (Moore 1998). Because a higher CEC usually indicates more clay and organic matter is present in the soil, high CEC soils generally have greater water holding capacity than low CEC soils. Soils dominated by clays with variable surface charge are typically strongly weathered. The fertility of these soils decreases with decreasing pH, which can be induced by acidifying nitrogen fertilizer, nitrate leaching, and clearing and agricultural practices (McKenzie *et al*. 2004). Soil pH change can also be caused by natural processes such as the decomposition of organic matter and leaching of cations. The lower the CEC of soil, the faster the soil pH will decrease with time. Consequently, the second strategy that can be done is to provide fertilizer and liming. However, lime should not be used excessively for a long time because it can increase the amount of positive charge into the soil (da Costa et al. 2016).

## Conclusion

Based on the colloidal charge characteristics, it can be concluded that four soil pedons in the hilly drylands of Aceh Besar include the variable charge soil, which is characterized by a negative surface charge with PZC <pH $H_2O$ and has a CEC the soil that is pH-dependent. PZC values of soil vary from 3.21 - 5.26. High PZC values are found in Eutric Hydrudands (Andisols) Saree and Plintic Kandiudox (Oxisols) Lembah Seulawah. In

*doi: 10.13170/aijst.9.2.17565*

contrast, low PZC values are found in Lithic Udorthents (Entisols) Jantho and Oxic Dystrudepts (Inceptisols) Cucum. Potential CEC varies from low to high (12.8 - 34.4 cmol $kg^{-1}$), while ECEC varies from very low to moderate (2.72 - 8.66 cmol $kg^{-1}$). The difference between PZC-pH and ΔpH is negatively correlated with the soil CEC, whereas they are positively correlated with permanent charge (pc) and pH $H_2O$. The soil CEC does not correlate directly with the amount of variable charge, PZC, and SOM. To improve soil quality in hilly dryland soils in Aceh Besar District can be done by decreasing the PZC status of soils with organic amendments and fertilizers or increase the pH by using liming.

## Acknowledgment

The authors would like to thank the technicians of the Laboratory of Soil and Plant Testing, Faculty of Agriculture, Universitas Syiah Kuala, Banda Aceh, where they were processed for analysis. The authors also thank Rector of Universitas Syiah Kuala and Head of LP2M (Lembaga Penelitian dan Pengabdian Kepada Masyarakat) Universitas Syiah Kuala for support and grant funding.

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